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An archaeometric investigation of glass beads decorating the reliquary of Saint Simètre from Lierneux, Belgium

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ABSTRACT

The reliquary of Saint Simètre (or Symètre), which is exposed in the Saint André church of Lierneux, was produced during the middle of the 13th century. It is made of a wooden chest with a roof (77 × 28 × 39 cm) covered by silver and golden copper, and decorated by 39 stones which were analysed by Raman and pXRF techniques to determine the nature of colouring agents and of raw materials. The results confirm the identification of 39 glass beads with green, blue, red or pink colours and showing a simple cutting. They show a lead silicate composition (45–55 wt% PbO) with a high level of potassium (5–10 wt% K_2O), and iron, cobalt, manganese and/or copper as coloring agents. The silver samples contain 98 wt% of Ag, and the golden border contains approximately 85 wt% of Cu and 14 wt% of Au. The brass decorations on the roof shows an average of 68 wt% of Cu and of 29 wt% of Zn. This study confirms that lead glass beads are contemporary to the reliquary and imported from central Europe.

1. Introduction

Simètre (or Symètre) was born in Lierneux at the beginning of the 2nd century. According to legend, he died of illness during his childhood before being resurrected by the bishop Saint Materne, who entrusted him to his uncle for giving him a Christian education. In adulthood, Simètre undertook a pilgrimage to Rome to venerate the relics of Saint Peter and Saint Paul, and met there the pope Pie I, who appointed him as a priest (Pairoux, 1988; Jehenson, 1992). On May 26th, 159, he died as a martyr in Rome during the celebration of the Eucharist, killed by Roman soldiers. The relics were brought back to Stavelot-Lierneux by the Abbot of Stavelot, Babolin (or Babolène), probably during the relics migration period between the 8th and 9th centuries. After this event, his cult increased highly, even though no miracle has been attributed to him, unlike the majority of other saints (George, 1987; Pairoux, 1992; George, 1992).

The reliquary of Saint Simètre (Fig. 1), exposed in the Saint André church of Lierneux, was produced during the middle of the 13th century (Pairoux, 1992; George, 1992; Van den Bossche, 1992a). It was created to commemorate the triumph of Saint Remacle, as shown by some silver plates on the roof (Jehenson, 1992). The reliquary is constituted by a wooden chest with a roof, measuring 77 cm in length, 28 cm in depth and 39 cm in height. It is covered by 14 silver plates decorated by silver or golden copper bands, and by coloured stones: 10 blue, 11 red, 9 green and 9 pink. On the length, several apostles as Saint Peter are represented on the chest, and narrative scenes or one text surrounded by angels are illustrated on the roof. One gable shows Christ on the cross, surrounded by the Virgin Mary and Saint John (Fig. 1B), and the other gable shows Virgin with the child on its side (Fig. 1C). A metallic border and three knobs also decorate the roof (Fig. 1A–C) (Van den Bossche, 1992a,b; Van den Bossche, 2005).

The development of portable XRF and Raman spectrometers has induced an increasing number of archaeometric studies focused on ancient goldsmith's items, as for example the Prague sceptre (Petrová et al., 2012), the Messina and Paolo Orsi jewellery collections (Barone et al., 2015, 2016), and the reliquary-bust of Saint Lambert (Bruni et al., 2019). In this paper, we present the results of a Raman and pXRF study of the reliquary of Saint Simètre (Lierneux, Belgium), with a special attention on the glass beads decorating the surface of this item. The chemical signatures of the glass beads will help us to shed some light on the colouring methods and on the raw materials used to manufacture this precious Mosan religious artwork.

2. Materials and methods

The Saint Simètre reliquary was investigated by portable Rama and

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Fig. 1. Photographs of the reliquary of Saint Simètre. (A) Lateral view. (B) Front view. (C) Back view.

X-ray fluorescence spectrometries, since this precious item cannot be easily moved. With these techniques, we analysed thirty-nine glass beads with various colours, rectangular shapes, and simple cuttings, which are localized on the roof and on the four lateral sides of the reliquary.

The portable Raman spectrometer is an Enwave Optronics EZRAMAN-I-DUAL instrument, loaned by the European centre of Archaeometry of Liège (Belgium). It is equipped with an optic fibre, and two light sources with different wavelengths are available: a green Nd:YAG laser (532 nm) and a red diode source (785 nm). The spot diameter of the optic fibres is approximately 6 mm, and the detector is of CCD type. The visible light beam is protected from ambient light sources by a rubber tip, which is placed as close as possible from the sample surface. The power of the spectrometer can be adjusted to a maximal value reaching 400 mW for the 785 nm source, and 100 mW for the 532 nm source; only 10% of the maximal power was used in our analyses. The measured spectra cover a wavelength range between 100 and 3200–4000^{-1}, and the resolution is of 7–8 cm^{-1}, depending on the wavelength. Duration of analysis was of 60 to 120 s. The final spectra were cut at 1400 cm^{-1} (spectral region between 100 and 1400 cm^{-1}); and they were not affected by any post-acquisition data manipulation. The comparative Raman spectra came mainly from Robinet et al. (2008) for glass beads.

The portable X-ray fluorescence spectrometer (pXRF) is a Thermo Fischer Niton XL3t, equipped with a 'GOLDD' detector, from the Mineralogy Laboratory, University of Liège (Belgium). X-rays are produced with a silver anode, using an acceleration voltage of 50 kV and a current of 200 μA; the spot size shows a diameter of 3 mm. Chemical elements were analysed from Mg (the lightest detectable element), but without a helium flow, this element cannot be detected with a good accuracy. Four filters were successively used in the analysis procedure, to select different ranges of wavelengths; the total counting time was 75 s per analysis point. The software utilizes a Fundamental Parameters algorithm to determine concentrations of each element. The concentration values were multiplied according to a standard element oxide conversion table, to produce a percentage by weight of each oxide, and then the values were normalized to 100 wt%.

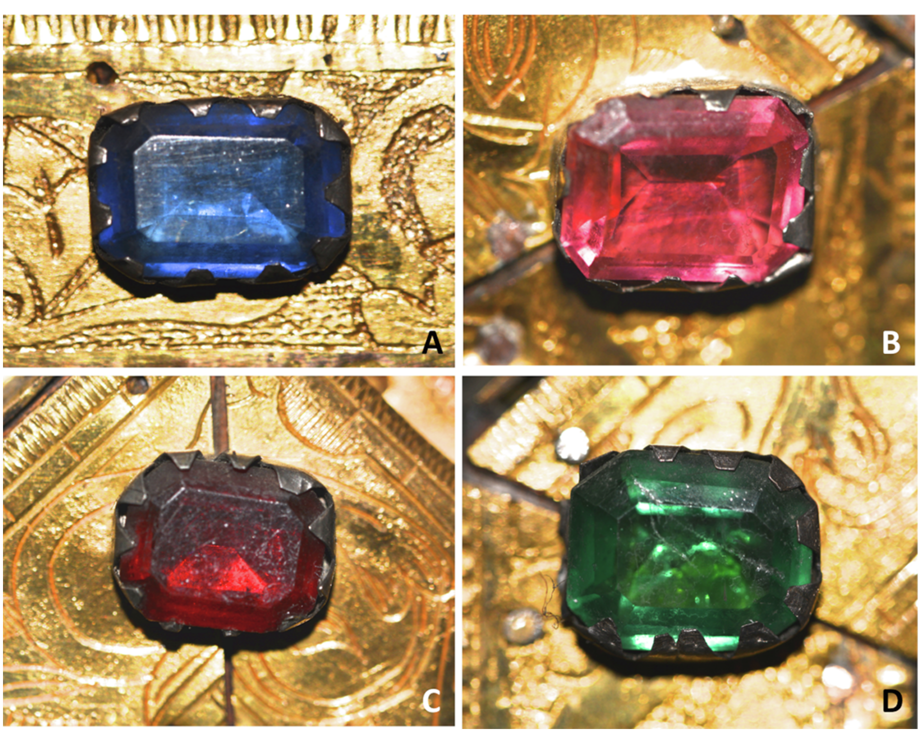

Fig. 2. Detailed pictures of the stones occurring on the reliquary of Saint Simètre. (A) Blue glass bead, with a simple cutting, set with eleven hooks # D10. (B) Pink glass bead showing a simple cutting. This rectangular stone is still set by five hooks # Ar2. (C) Rectangular red glass bead set by eleven hooks # Av1. (D) Green glass bead still set by nine hooks # Ar3.

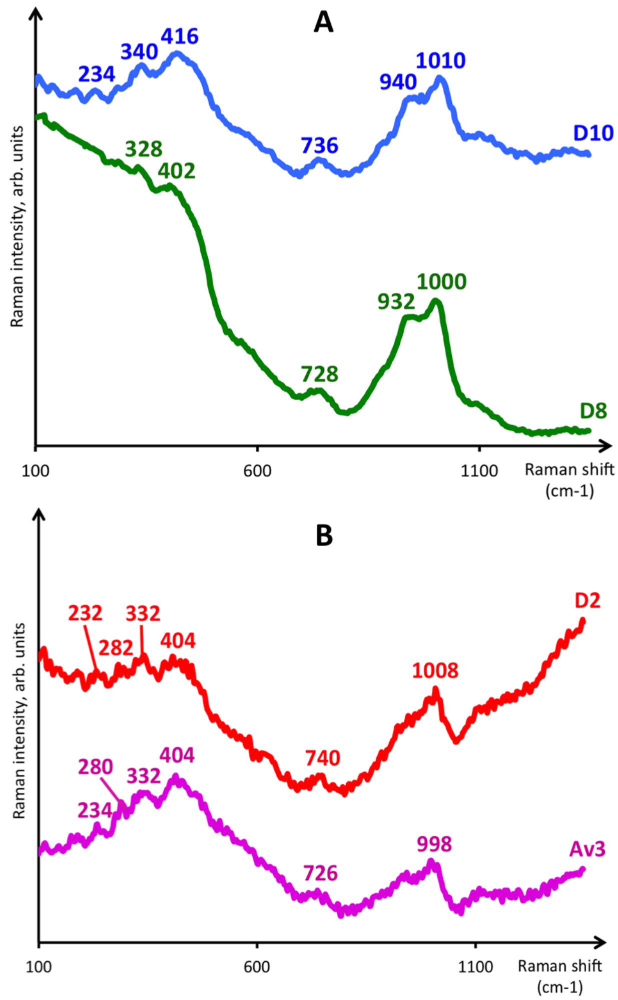

Fig. 3. Raman spectra of the stones decorating the reliquary of Saint Simètre. (A) Blue glass beads (# D10), green glass beads (# D8). (B) Red glass beads (# D2) and pink glass beads (# Av3).

3. Results and discussion

3.1. Description of glass beads

The reliquary is decorated by 39 glass beads: 16 are localized on the roof, 9 on the both widths, and 14 on the both lengths (Fig. 1; the exact nomenclature and position of the stones is available online as Supplementary material). The stones show rectangular shapes (approximately 1.2 × 1.7 cm), with simple cuttings and various colours: 10 blue, 9 pink, 11 red and 9 green. Stones occur in silver settings, fixed with many hooks located all around the rectangular stones (Fig. 2A–D).

3.2. Raman spectra and correlation with glass composition

Some stones of each colour have been analysed. The high values of fluorescence and absorption in dark-coloured stones made the analyses sometimes difficult to obtain. These phenomena are common in handheld instrumentation (Jehlička et al., 2011). A list of the Raman bands observed for all samples is available as Supplementary material (Table 3).

The spectra of blue, green, red and pink stones are quite similar (Fig. 3A and B), characterized by broad bands, confirming the amorphous nature of these phases. All glass beads contain a main band located between 998 and 1010 cm^{-1}, showing a relatively small Raman intensity. Depending on spectra, minor bands are situated at approximately 332, 404 and 726 cm^{-1}. These spectra are in good agreement with Raman signatures spectra of lead-alkali silicate glasses from Robinet et al. (2008).

3.3. Chemical characterization

Chemical analyses of the stones and noble metals are given in Tables 1 and 2. Some analyses were omitted because of their poor quality. Sodium was not measured, but it can be considered as absent in lead glass beads, in agreement with the Raman spectra and previous analyses (Dungworth and Brain, 2009). Arsenic was impossible to measure in Pb-bearing glass, due to an XRF interference between these chemical elements. Nickel, strontium and tin are below the detection limit.

All glass beads show relatively similar compositions with high amounts of PbO (ca. 42 to 55 wt%), SiO_2 (ca. 29 to 40 wt%), and K_2O (ca. 4–9 wt%), as well as small amounts of CaO (ca. 0.4–1.4 wt%) (Fig. 4A–C). However, two groups can be distinguished: the red and pink beads that contain lower amounts of CaO and K_2O (CaO ~ 0.5 to 1 wt% and K_2O ~ 4 to 6 wt%), and the green and blue beads that contain higher amounts of these elements (CaO ~ 0.5 to 1.5 wt% and K_2O ~ 5 to 9 wt%) (Fig. 4A–C; Table 1). According to the classification proposed by Schalm et al. (2007), these glasses correspond to lead glass.

Analyses of noble metals (Table 2) indicate that silver samples, constituting the plates (# Nm2) or the angels (# Nm8), contain 97–98 wt% Ag. The metallic border (# Nm5) and the knobs (# Nm6) decorating the roof are made of brass, with 65 to 71 wt% Cu and 26–33 wt% Zn. The decorative golden bands (# Nm1) contain 85 wt% Cu and 14 wt% Au, in agreement with the golden copper composition in the literature (Van den Bossche, 1992a,b; Van den Bossche, 2005). The golden decoration around the different figures, and the wipe in the pelvis of Jesus (# Nm3), are composed of electrum, with 64 wt% Au and 35 wt% Ag.

3.4. Relationships between chemical composition and glass colour

The chemical data determined by pXRF give us fundamental data to identify the materials used for the coloration of glass beads. The most common colouring agents are copper (green), iron (green) and cobalt (blue) ions, copper metal nanoparticles (red), and lead-based pigments dispersed in glass (yellow). Aluminium and manganese are often occurring as impurities in quartz or sand, but manganese can also be used as decolourizer or colouring agent to obtain pink or purple hues (Cannella, 2006; Verità, 2014; Colomban, 2019).

Blue glass beads show cobalt, zinc and copper contents in the ranges 0.12–0.15 wt% CoO, 0.09–0.13 wt% ZnO, and 0.03–0.07 wt% CuO (Table 1). The divalent cobalt, used since the Late Bronze Age, is one of the most powerful and stable colouring agents. Very small amounts, even below 0.05 wt%, are sufficient to already give a noticeable blue coloration to a glass (Cannella, 2006, p. 163-164; Giannini et al., 2017). Some trace elements are associated to cobalt as zinc, arsenic or nickel. These ones permit to establish hypothesis about the localisation of the cobalt deposits (Gratuze et al. 1992; Giannini et al., 2017). The blue glass beads on the reliquary contain approximately 0.11 wt% ZnO and no nickel (Table 1). Arsenic was not measured by pXRF (see 3.3), but the As-O bond at 820 cm^{-1} (Mulvihill et al., 2008) was not detected in the Raman spectra (Fig. 3A), indicating that arsenic is probably not present in blue glass beads. These results are in agreement with the geochemical signature of European cobalt-zinc deposits (Gratuze et al. 1992).

Green glass beads are characterized by high amounts of Fe_2O_3 (1.13–2.14 wt%) and CuO (0.72–1.30 wt%). Both are responsible for the emerald coloration (Cannella, 2006, p. 186-187; Cottam and Jackson, 2018), as in dark green Venetian glass from Verità (2013) and from Bruni et al. (2019).

Red glass beads contain some copper reaching 0.49–0.71 wt%. Copper nanoparticles (Cu^0), dispersed as precipitates in the glassy

Table 1
Chemical composition of glass beads decorating the shrine of Saint Symètre.

Sample	*Phase*	*Colour*	*MgO*	*Al_2O_3*	*SiO_2*	*P_2O_5*	*SO_3*	*Cl*	*K_2O*	*CaO*	*TiO_2*	*MnO*	*Fe_2O_3*	*CoO*	*CuO*	*ZnO*	*Sb_2O_3*	*PbO*
Av5	Glass	Blue	–	1.49	**37.38**	**2.10**	0.68	0.79	**7.82**	0.88	–	0.26	–	0.13	0.03	0.09	0.48	**47.87**
D5	Glass	Blue	–	1.33	**39.43**	**2.15**	1.58	0.65	**6.92**	1.18	–	0.21	–	0.13	0.03	0.09	0.33	**45.97**
D10	Glass	Blue	–	1.39	**36.95**	**2.11**	0.74	0.75	**9.19**	0.50	–	0.33	–	0.15	0.04	0.11	0.47	**47.28**
D15	Glass	Blue	–	1.99	**35.41**	1.65	1.49	0.50	**7.95**	0.72	–	0.26	–	0.14	0.06	0.10	0.63	**49.10**
G2	Glass	Blue	–	**2.28**	**36.29**	1.84	1.12	0.67	**7.05**	**2.03**	–	0.26	–	0.13	0.03	0.10	0.39	**47.80**
G5	Glass	Blue	–	1.52	**37.22**	**2.00**	0.56	0.64	**7.32**	1.30	–	0.23	–	0.12	0.03	0.12	0.35	**48.59**
G6	Glass	Blue	–	0.90	**36.65**	**2.14**	1.65	0.67	**7.39**	0.36	–	0.25	–	0.13	0.03	0.13	0.42	**49.28**
G7	Glass	Blue	–	**2.45**	**42.20**	**2.31**	0.91	0.60	**6.66**	1.42	–	0.19	–	0.12	0.07	0.11	0.42	**42.54**
Av2	Glass	Green	–	1.33	**34.46**	1.86	1.13	0.60	**5.71**	0.57	–	0.19	1.39	–	1.14	–	0.34	**51.27**
D6	Glass	Green	–	**3.03**	**31.83**	**2.66**	1.46	0.78	**5.11**	0.71	–	0.22	1.44	–	0.72	–	0.18	**51.88**
D8	Glass	Green	–	1.99	**35.16**	**2.41**	0.77	0.72	**5.44**	0.69	–	0.20	1.51	–	1.38	–	0.18	**49.57**
D12	Glass	Green	–	1.88	**33.95**	**2.04**	1.14	0.56	**6.13**	0.63	–	0.19	1.62	–	1.25	–	0.18	**50.42**
D13	Glass	Green	–	1.88	**29.00**	1.44	1.08	0.45	**9.40**	1.26	–	0.23	**2.14**	–	1.30	–	0.26	**51.56**
D16	Glass	Green	–	1.53	**35.33**	**2.38**	0.69	0.71	**8.39**	0.67	–	0.19	1.67	–	0.85	–	0.21	**47.38**
Ar3	Glass	Green	–	1.43	**37.08**	**2.43**	0.40	0.75	**5.48**	0.50	–	0.19	1.61	–	1.01	–	0.14	**48.98**
G4	Glass	Green	–	**3.54**	**34.80**	**2.14**	0.75	0.75	**5.32**	0.62	–	0.14	1.13	–	0.85	–	0.28	**49.69**
Av1	Glass	Red	1–5	1.14	**33.08**	1.74	1.33	0.64	**5.20**	0.74	–	0.17	–	–	0.49	–	0.85	**51.70**
Av4	Glass	Red	1–5	1.02	**34.13**	**2.92**	1.35	0.63	**5.81**	0.83	–	0.20	–	–	0.60	–	0.59	**49.36**
D2	Glass	Red	1–5	**2.19**	**36.28**	**2.18**	1.19	0.63	**4.98**	0.72	–	0.19	–	–	0.55	–	0.62	**47.62**
D3	Glass	Red	1–5	0.97	**34.08**	**2.10**	1.26	0.71	**3.91**	0.77	–	0.18	–	–	0.67	–	0.85	**50.97**
Sample	*Phase*	*Colour*	*MgO*	*Al_2O_3*	*SiO_2*	*P_2O_5*	*SO_3*	*Cl*	*K_2O*	*CaO*	*TiO_2*	*MnO*	*Fe_2O_3*	*CoO*	*CuO*	*ZnO*	*Sb_2O_3*	*PbO*
D4	Glass	Red	1–5	1.67	**31.20**	1.84	1.05	0.59	**5.10**	0.83	–	0.16	–	–	0.53	–	0.90	**53.34**
D11	Glass	Red	1–5	1.29	**31.65**	1.37	1.11	0.64	**6.29**	0.79	–	0.26	–	–	0.51	–	0.96	**51.75**
D14	Glass	Red	1–5	**2.01**	**32.66**	1.63	1.35	0.51	**4.21**	0.79	–	0.21	–	–	0.61	–	0.87	**50.31**
Ar1	Glass	Red	1–5	1.73	**33.19**	**2.53**	1.34	0.89	**4.12**	0.92	–	0.23	–	–	0.71	–	0.53	**50.34**
G1	Glass	Red	1–5	**3.47**	**31.35**	1.86	1.21	0.63	**5.07**	0.72	–	0.27	–	–	0.59	–	0.81	**50.05**
Av3	Glass	Pink	1–5	1.70	**31.97**	**2.17**	0.94	0.62	**5.07**	0.37	–	1.11	–	–	0.05	–	0.25	**53.74**
D1	Glass	Pink	1–5	1.35	**34.67**	1.82	1.01	0.57	**3.97**	0.55	–	1.06	–	–	0.10	–	0.23	**51.78**
D7	Glass	Pink	1–5	1.00	**33.10**	**2.04**	1.03	0.56	**4.65**	0.49	–	1.31	–	–	0.06	–	0.25	**52.20**
D9	Glass	Pink	1–5	1.36	**34.44**	1.90	0.74	0.62	**5.00**	0.43	–	1.18	–	–	0.04	–	0.24	**50.97**
Ar2	Glass	Pink	1–5	1.49	**30.19**	**2.05**	0.79	0.61	**4.62**	0.53	–	1.14	–	–	0.07	–	0.21	**54.66**
G3	Glass	Pink	1–5	**2.34**	**30.48**	**2.06**	0.83	0.51	**4.43**	0.54	–	1.09	–	–	0.11	–	0.22	**54.11**

Analyses realized by pXRF, data presented as wt. % of oxides, normalized to 100 wt%. -: Below detection limit or not analysed. Percentages above 2 wt% are shown in bold.

Table 2
Chemical compositions of noble metals constituting the shrine of saint Symètre.

Sample	Ag	Au	Pb	Zn	Cu	Fe	Ni	Co	Sn
Nm1	0.10	**14.23**	0.48	0.15	**84.99**	0.05	–	–	–
Nm2	**97.68**	0.07	0.10	0.18	1.93	–	0.04	–	–
Nm3[1]	**34.36**	**63.73**	0.58	–	1.33	–	–	–	–
Nm4	**97.48**	0.43	0.66	–	1.32	–	0.11	–	–
Nm5	0.07	1.41	0.40	**26.55**	**71.16**	0.41	–	–	–
Nm6	0.04	0.79	0.48	**33.13**	**65.51**	–	0.05	–	–
Nm7	**98.21**	–	0.11	0.15	1.45	0.03	0.06	–	–
Nm8[2]	**97.04**	0.53	0.42	0.05	1.72	0.24	–	–	–

Analyses realized by pXRF, data presented as wt. % of elements, normalized to 100 wt%. -: Below detection limit. Percentages above 2 wt% are shown in bold.
[1] : Golden zone on the wipe around the pelvis of Jesus.
[2] : Angel around the plate with a text.

Table 3
List with all Raman bands of glass beads. Numbers in bold denote strong bands.

Sample	Phase	Colour	Raman peaks/bands (cm^{-1})
Mav3	Glass	Blue	324; 402; 514; 716; 866; 1050
D10	Glass	Blue	234; 340; 416; 736; 940; **1010**
Av5	Glass	Blue	232; 270; 338; 426; 670; 730; 946; **1008**
D5	Glass	Blue	230; 276; 340; 418; 746; 950; **1006**
G5	Glass	Blue	236; 334; 416; 734; **996**
D8	Glass	Green	330; 402; 728; 932; **1000**
Av2	Glass	Green	228; 280; 338; 402; 726; **998**
D6	Glass	Green	330; 396; 730; 932; **1004**
D2	Glass	Red	232; 282; 332; 406; 740; **1008**
Av1	Glass	Red	236; 332; 402; 1004
Av4	Glass	Red	340; 408; 730; 1006
Av3	Glass	Pink	234; 280; 332; 404; 726; 934; **998**
D1	Glass	Pink	236; 284; 338; 406; 734; **1008**
D9	Glass	Pink	232; 282; 340; 406; 740; **1008**

matrix, are responsible for the red colour in sufficiently reducing condition. The particles of metallic copper must be quite small (between 20 and 100 nm) and widely spaced to develop a translucent ruby red colour (Cannella, 2006p. 146; Kunicki-Goldfinger et al., 2014).

Pink glass beads show higher amounts of MnO (1.06 to 1.31 wt%) and lower amounts of CuO (0.04–0.11 wt%). When its content is higher than 0.5 wt%, divalent manganese is not considered as an impurity, and gives a pink hue (Cannella, 2006, p. 175).

3.5. Origin and dating of glass beads

Gemstones have always been fascinating due to their colours, brilliances and rarities, giving them a great value. They were used as medium of exchange or decoration and, very soon in History, they were imitated by cheaper coloured glass beads (Cannella, 2006). After a restoration on ancient items, gems or glass beads can also be exchanged with more recent glass beads. This modification of original stones is identified with Raman spectra, using the absolute intensity of the Raman scattering, especially the band located at about 1000 cm^{-1}. Indeed, medieval glass beads often have a weathering surface due to pollution, preventing a good penetration of the laser light, even in the museum (Robinet et al., 2008; Colomban, 2008; Tournié et al., 2008). The glass beads on the reliquary of Saint Simètre show relatively flat Raman spectra, with low intense bands at 1000 cm^{-1}. These ones are therefore ancient, with an altered layer occurring at their surface.

In Europe, simple faceting, with a large square or rectangular table surrounded by some facets, is known since the Middle Ages. From the 14th century, more complex faceting techniques progressively appeared (Brose, 1954; Klein, 2005). The 39 glass beads observed on the

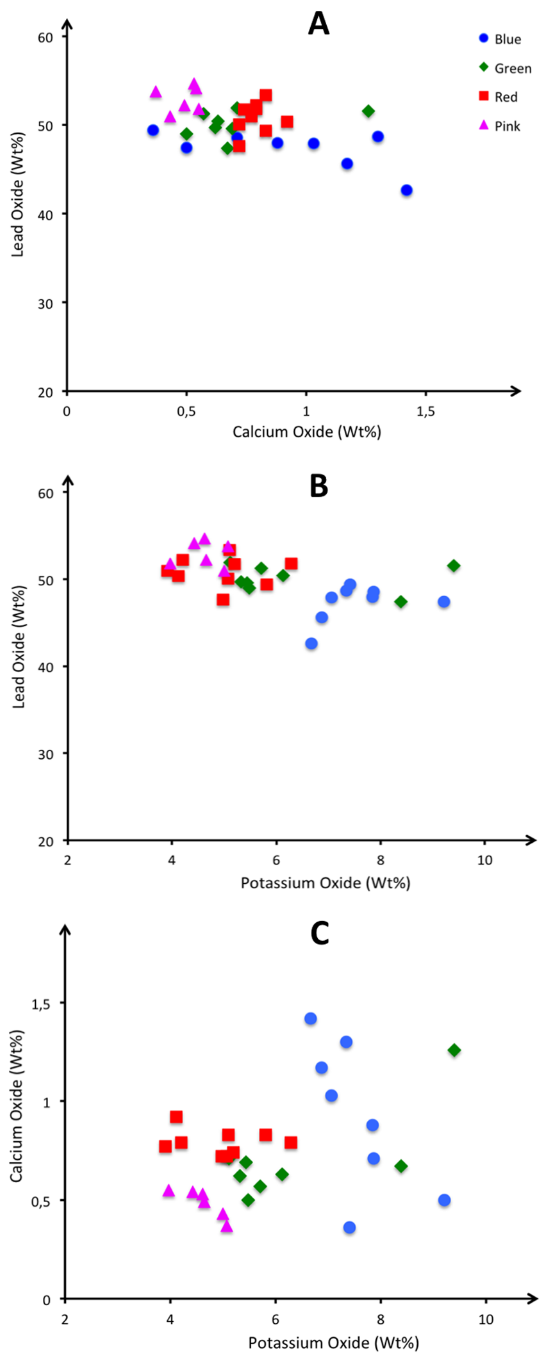

Fig. 4. Correlations between some oxide contents in the glass beads from the reliquary of Saint Simètre, determined by pXRF. (A) PbO *vs* CaO. (B) PbO *vs* K_2O. (C) CaO *vs* K_2O.

reliquary of Saint Simètre show a simple cutting, with a large table and several surrounding facets (Fig. 2A–D); this cutting technique is similar to that recently observed on the reliquary bust of Saint Lambert in Liège (Bruni et al., 2019). These simple faceting techniques are typical for ancient glass beads; as a consequence, all glass beads observed on the reliquary of Saint Simètre can be considered as contemporaneous with its manufacture in the middle of the 13th century (Pairoux, 1992; George, 1992; Van den Bossche, 1992a).

Blue glass beads contain both CoO and ZnO, in amounts reaching 0.13 and 0.11 wt%, respectively. The Co-Zn ores with low levels of manganese (0.25 wt%) correspond to European deposits. These ores, used approximately between the 13th and the 14th century, could originate from the Freiberg deposits in Germany, which were mined at the end of the 12th century onward (Gratuze et al., 1992; Giannini et al., 2017), or from Syria (Cannella, 2006).

Mecking (2013) has compared the chemical composition of six lead glasses – high-lead glass, wood-ash lead glass, lead smoother, soda-lead glass, Slavic lead glass, and central Europe lead-ash glass – which have different European origins. The lead glasses of “central Europe lead-ash glass”, with an average content of 52 wt% PbO and 9 wt% K_2O, are closest to those of Saint Simètre which contain an average of 50 wt% PbO and 6 wt% K_2O. The CaO/K_2O ratio is also in good agreement with the value between 0.009 and 0.360 for the “central Europe lead-ash glass”. These lead glasses come from Germany, Austria, Switzerland, and Czech Republic (Mecking, 2013).

4. Conclusions

The reliquary of Saint Simètre is decorated by 39 blue, green, pink or red colored stones, with a simple cutting. The chemical analyses show a lead silicate composition, with a high level of potassium and different coloring agents as cobalt, iron, copper or manganese. Due to their chemical composition, Raman intensity and simple faceting, the lead glass beads are contemporary to the reliquary, and were imported from central Europe. The silver samples contain 98 wt% Ag, and the golden border approximately 85 wt% Cu and 14 wt% Au. The brass decorations on the roof indicate an average of 68 wt% Cu and 29 wt% Zn. The archaeometric investigation of religious goldsmith artwork, with non-destructive techniques as pXRF or Raman spectrometry, is a necessary step to better understand the historical and geographic contexts in which these objects were produced.

Acknowledgments

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Appendix A. Supplementary data

Supplementary data to this article can be found online at https://doi.org/10.1016/j.jasrep.2020.102451.

References

Barone, G., Bersani, D., Jehlicka, J., Lottici, P.P., Mazzoleni, P., Raneri, S., Vandenabeele, P., Di Giacomo, C., Larinà, G., 2015. Nondestructive investigation on the 17–18th centuries Sicilian jewelry collection at the Messina regional museum using mobile Raman equipment. J. Raman Spectr. 46, 989–995.

Barone, G., Mazzoleni, P., Raneri, S., Jehlicka, J., Vandenabeele, P., Lottici, P.P., Lamagna, G., Manenti, A.M., Bersani, D., 2016. Raman investigation of precious jewelry collections preserved in Paolo Orsi regional museum (Siracusa, Sicily) using portable equipment. Appl. Spectr. 70, 1420–1431.

Brose, H.W., 1954. A Short History of Faceting. Lapid. J. 2, 446–452.

Bruni, Y., Hatert, F., George, P., Strivay, D., 2019. The Reliquary bust of Saint Lambert from the Liège cathedral, Belgium: gemstones and glass beads analysis by pXRF and Raman spectroscopy. Archaeometry in press.

Cannella, A.-M., 2006. Gemmes, verre coloré, fausses pierres précieuses au Moyen Age. Le quatrième livre du « Trésorier de Philosophie naturelle des pierres précieuses » de Jean d’Outremeuse, Librairie Doz, Genève, 480 p.

Colomban, P., 2008. On-site Raman identification and dating of ancient glasses: A review of procedures and tools. J. Cult. Her. 9, e55–e60.

Colomban, P., 2019. Colouring agents fo Glass, Glaze and Enamel : Tracing Innovation and Exchange Routes. In P. Vandenabeele and H. Edwards (Eds.), Raman Spectroscopy in Archaeology and Art History. Royale Society of Chemistry, Vol. 2, supplementary information, London, UK.

Cottam, S., Jackson, C., 2018. Things that travelled: Precious things for special people? In: Rosenow, D., Phelps, M., Meek, A., Freestone, I. (Eds.), Things that travelled. UCL Press, London, pp. 92–106.

Dungworth, D., Brain, C., 2009. Late 17^{th} century crystal glass: An analytical investigation. J. Glass Stud. 51, 111–137.

George, P., 1987. Documents inédits sur le trésor des reliques de l’abbaye de Satvelot-Malmedy et dépendances (IXe-XVIIIe siècle). Bull. Comm. Royale Hist. 153 (2), 65–108.

P. George E. Van den Bossche Patrimoine religieux du Pays de Lierneux 1992 692–1992, pp. 16–27.
Giannini, R., Freestone, I.C., Shortland, A.J., 2017. European cobalt sources identified in the production of Chinese fammille rose porcelain. J. Archaeol. Sci. 80, 27–36.
Gratuze, B., Soulier, I., Barradon, J.N., Roy, D., 1992. De l'origine du cobalt dans les verres. Rev. Archaéom. 16, 97–108.
Jehenson, G., 1992. Lierneux au fil du temps: 692–1992. Admin. Comm, Lierneux, pp. 88.
Jehlička, J., Culka, A., Vandenabeele, P., Edwards, H.G.M., 2011. Critical evaluation of a handheld Raman spectrometer with near infrared (785 nm) excitation for field identification of minerals. Spectr. Acta A80, 36–40.
Klein, G., 2005. Faceting History: cutting diamonds & colored stones. Xlibris Corporation, USA, pp. 242.
Kunicki-Goldfinger, J.J., Freestone, I.C., McDonald, I., Hobot, J.A., Gilderdale-Scott, H., Ayers, T., 2014. Technology, production and chronology of red window glass in the medieval period – rediscovery of a lost technology. J. Archaeol. Sci. 41, 89–105.
Mecking, O., 2013. Medieval lead glass in Central Europe. Archaeom. 55, 640–662.
Mulvihill, M., Tao, A., Benjauthrit, K., Arnold, J., Yang, P., 2008. Surface-enhanced raman spectrometry for trace arsenic detection in contamined water. Angewandte Chem. Internat. Ed. 47, 6456–6460.
Pairoux, A., 1988. Une vie inédite de saint Simètre de Lierneux (XIVe siècle). Bull. Comm. Royale Hist. 154, 199–226.
Pairoux, A., 1992. Saint Simètre de Lierneux. In : Van den Bossche, B. (Ed.), Patrimoine religieux du Pays de Lierneux : 692-1992, pp. 9-11.
Petrová, Z., Jehlicka, J., Capoun, T., Hanus, R., Trojek, T., Goliás, V., 2012. Gemstones and noble metals adorning the sceptre of the Faculty of Science of Charles University in Prague: integrated analysis by Raman and XRF handheld instruments. J. Raman Spectr. 43, 1275–1280.
Robinet, L., Bouquillon, A., Hartwig, J., 2008. Correlations between Raman parameters and elemental composition in lead and lead alkali silicate glasses. J. Raman Spectr. 39, 618–626.
Schalm, O., Janssens, K., Wouters, H., Caluwé, D., 2007. Composition of 12–18th century window glass in Belgium: Non-figurative windows in secular buildings and stained-glass windows in religious buildings. Spectrochem. Acta B62, 663–668.
Tournié, A., Ricciardi, P., Colomban, P., 2008. Glass corrosion mechanisms: A multiscale analysis. I. Solid State Ion. 179, 2142–2154.
B. Van den Bossche B. Van den Bossche Patrimoine religieux du Pays de Lierneux 1992 692–1992, pp. 28–41.
B. Van den Bossche. Catalogue. In Van den Bossche, B. Patrimoine religieux du Pays de Lierneux 1992 692–1992 pp., 44–50.
B. Van den Bossche S. Blick R. Tekippe Art and Architecture of the Medieval Pilgrimage in Northern Europe and the British Isles Textes 2005 649 667.
Verità, M., 2013. Venetian Soda Glass. In: In: Janssens, K. (Ed.), Modern Methods for Analysing Archaeological and Historical Glass Vol 1. Wiley, Chichester, pp. 515–536.
Verità, M., 2014. Secrets and innovations of Venetain glass between the 15th and 17th centuries: Raw materials, glass melting and artefacts. Atti dell' Instituto Veneto di Scienze, lettere ed arti 172, 53–68.